Structural changes in high-temperature synthesis of luminescent alumina ceramics

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Abstract. Scanning electron microscopy was used to study structural changes in luminescent alumina ceramics which was synthesized from nanopowder at high temperatures in reducing environment. An effect of synthesis parameters on size-distribution of grains, their shape and a number of pores in the samples under study was determined. It was found that in a certain temperature range grains are the same ones in the precursor nanopowder, which is associated with the emergence of nanoparticles of lower aluminum oxides.

1. Introduction

Possibilities to use nanosize materials to create luminophors with high light yield and their applications in optical electronics are studied today [1]. Physico-chemical and energetical characteristics of nanomaterials influence greatly their optical properties. Producing luminophors on the base of oxide ceramics synthesized at high temperatures in highly reducing environment is promising [2]. Such ceramics are very strong mechanically and their properties are stable [3]. Luminescence centers caused by oxygen vacancies form in these ceramics. However, high-temperature synthesis of luminescent ceramics is accompanied by changes in structure and growth of the grains [4]. The effects of synthesis conditions on ceramics structure and their luminescent characteristics are little studied. Thus, the aim of the work is to research structural changes in ultrafine alumina ceramics with varying parameters of pressing and sintering.

2. Materials and Methods

Experimental ceramic samples were synthesized from highly pure (99,997%) commercial α-Al_2O_3 nanopowder created by using an alcoholate method. The samples were pressed statically with Specac hydraulic press in metal press moulds under pressure from 450 to 550 MPa. Further, the ceramics were synthesized in a vacuum electric oven (10^{-2} Pa) at the presence and absence of carbon at varying temperatures from 1200 to 1700°C and with annealing for 0.5-5 hours.

The analysis of the particle size distributions of α-Al_2O_3 nanopowder is performed with the Nanophox proton cross correlation spectrometer based on dynamic light scattering. Nanophox provided the twofold detection by 2 laser beams which cross in the measuring volume and 2 detectors which collect the scaterring light. This allows us to select only the single scaterring light information within the total scaterring light under 90^0.

The surface structure and the volume (chip) of the samples were studied by using a scanning electron microscope (SEM) Zeiss Sigma VP. Fragments of ultrafine ceramic structures were analyzed with specialized SIAMS 700 software (SIAMS Photolab complex). This software enabled the quantity

characteristics of structural elements of the material to be found. The optical system and computer program of the analyzer allowed us to find all particles in each SEM microphoto and to determine their precise sizes (with tenths of nanometer precision). Particle size distribution for each sample type was defined on the analysis of over 1500 particles.

3. Results and discussion

Particle sizes were analysed by using a method of dynamic light scattering to find the size of structural elements in the precursor α-Al_2O_3 powder. Figure 1 shows SEM image (a) and particle size distribution (b) of α-Al_2O_3 powder. The measurements were repeated several times, so that a set of single measurements was obtained. It can be seen in the figure that a big proportion (> 80 %) in the sample is particles of the sizes 5-50 nm (indicated by arrows). A number of particles with sizes of 100-250 nm is not higher than 20 %. The statistical evaluation contains the absolute standard deviation of the single measurements for each particle size class. In this regard, maximal values up to approximately 20 % are possible and quite normal due to the principle of the applied measurement technique but never reached for any of the analyzed sample. The maximum of the standard deviation calculated for the measurements of this sample reveals a value below 10.9 %.

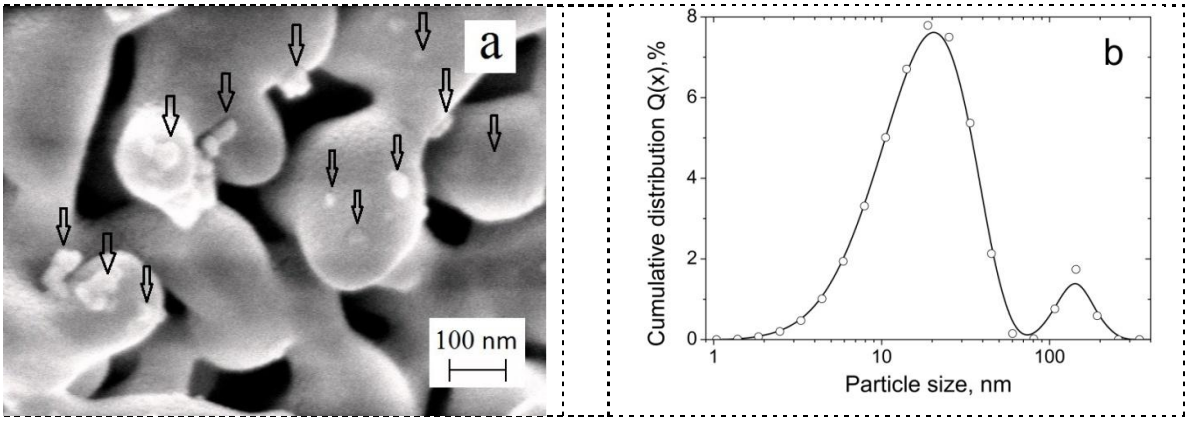

Figure 1. SEM image (a) and particle size distribution (b) of precursor α-Al_2O_3 powder.

To analyze the structure of the ceramic alumina samples synthesized at different heating modes, the obtained SEM microphotos were used. Particle size distributions were found for the samples under study, and the obtained dependences were analyzed. The following parameters were defined: a type and value of the maximum of grain size distribution, mean size and shape of grains. An increasing synthesis temperature leads to a decreasing number of pores and growing density of the samples.

Figure 2 shows SEM images of Al_2O_3 ceramics annealed at 1600 ºC for 1 hour with the presence of carbon (a) and with the absence of carbon (b). A highly pure graphite (99.99%) rod with the mass of 20 g was placed 5 mm from the samples in the vacuum chamber of the furnace. It was done to create a strong reducing medium which is needed to synthesize oxygen-deficient samples of alumina ceramics.

Oxygen vacancies create luminescence F-type centers [2]. The absence of carbon in the chamber made the grains grow significantly up to micron sizes. The basic structure was composed of the grains of 1-5 μm. However, the shape of the grains almost did not change. The synthesis of ceramics without carbon was accompanied by a significant decrease in porosity in comparison with the samples synthesized with the presence of graphite. Thus, in the samples annealed at 1700 ºC for 1 hour there were no pores at all. With the presence of graphite a layer structure of the sintered particles emerges. The sintered particles were up to 1 μm in size and of polyhedral shape with clearly discernable facets. It is noteworthy that with annealing at 1600 ºC for 1 hour there are no particles of the precursor powder (smaller than 250 nm), which indicates uniform sintering throughout bulk of ceramics.

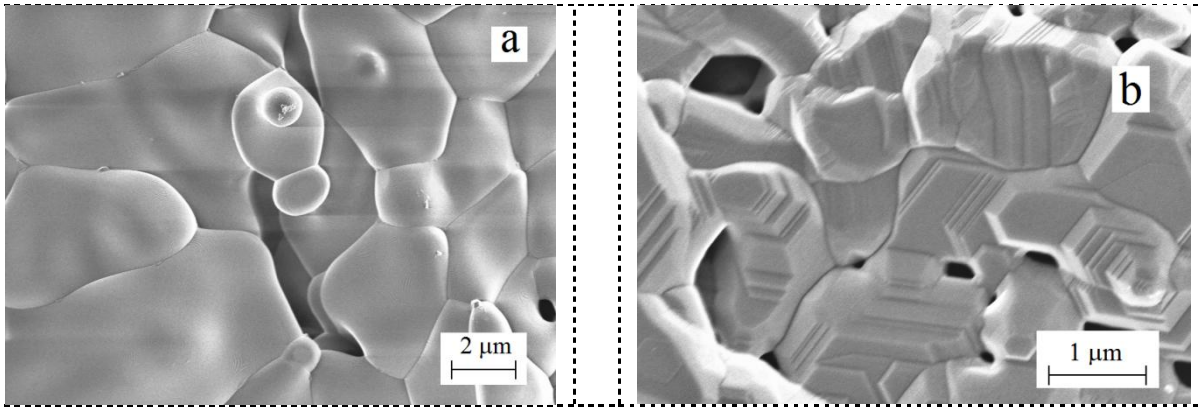

Figure 2. SEM image Al_2O_3 ceramics synthesized at 1600 °C for 1 hour with the absence (a) and presence (b) of carbon.

Figure 3 shows a typical SEM image of alumina ceramics synthesized at 1700°C for 30 minutes with the presence of carbon. The examining of the given microphotos allows us to conclude that as a result of high-temperature ceramics synthesis in vacuum, agglomerates with mean size of about 600-800 nm (Figure 3b) are formed. Figure 3a shows an image of single grains of about 600 nm in size, on the facets of which particles 100-200 nm and 10-40 nm in size were localized. It can be seen that small grains are tightly located along the perimeter of a bigger grain. The sizes of these particles are the same ones in the precursor nanopowder. Such differences in sizes can be explained by the processes of stoichiometric compositional disorder of oxygen at sintering with the presence of carbon. Big grains recrystallized from the precursor α-Al_2O_3 powder, and small grains might emerge from due to lower aluminium oxides (AlO, Al_2O), in which luminescent centers can be formed as well, which is verified by the data in [3]. Further analysis of X-ray diffraction patterns showed that phase ceramic composition does not change and is characterized by 100 % α-phase with the structural changes mentioned above.

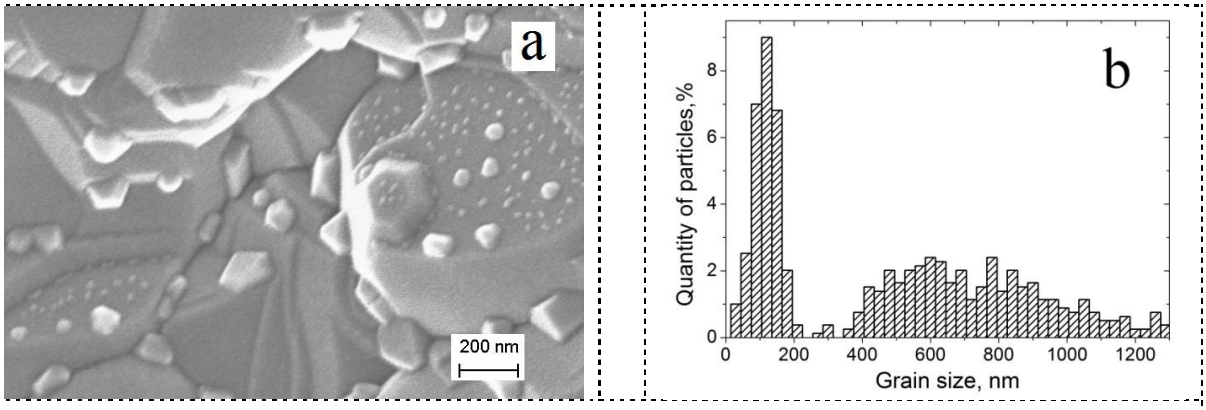

Figure 3. SEM-image (**a**) and grain size distribution (**b**) of ultrafine ceramics Al_2O_3 synthesized at 1700°C for 30 minutes with the presence of carbon.

When the samples are annealed for 1 hour (1700°C) there are no pores in the sintered ceramis including the cases with the presence of carbon (Figure 4). In this situation the surface of the grain facets become uneven. It has hollows with the dimensions comparable with those of the grains found at shorter annealing (Figure 3a). The hollows may be associated with deconvolution of alumina into lower oxides. This is confirmed by the fact that under annealing for over two hours the sample is

almost completely decomposed into volatile components including lower oxides which are removed with a vacuum system.

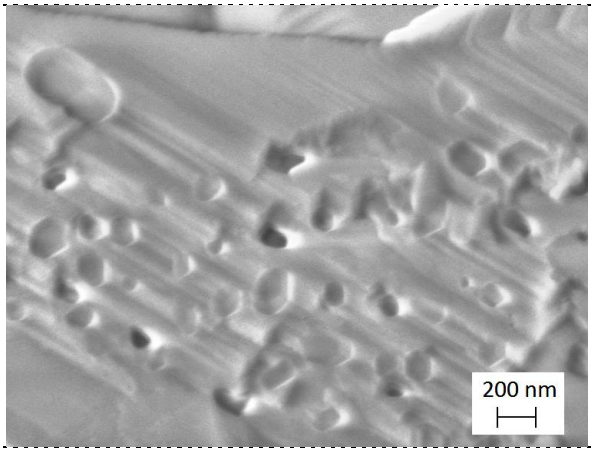

Figure 4. SEM-image ceramics Al_2O_3 synthesized at 1700°C (1 hour).

Photoluminescence (PL) spectra in the emission band of F-centers (420 nm) were analyzed in an express mode to estimate the effect of structure on luminescent yield of the material. It was found that the maximum concentration of luminescence centers is achieved at the highest temperature T=1700°C and annealing time t=1 h. Thus, synthesis of luminescent ceramics at the highest temperature and annealing time leads to two opposite effects: formation of the sample with maximal PL intensity and disorder of its geometrical dimensions down to its complete "burnout". Regarding this, the following optimal parameters for producing luminescent Al_2O_3 ceramics were chosen: synthesis temperature 1600 °C with annealing time over 2 hours.

4. Conclusion

The effect of the synthesis conditions on the structure of ultrafine oxygen-deficient Al_2O_3 ceramics was found. It was shown that with an increasing temperature of ceramics synthesis in vacuum, propotions of particles bigger than 250 nm and new particles of 10-40 nm increase. Luminescent properties also depend on the mode of sample synthesis. Optimal conditions for ceramics synthesis were found. They give a high photon yield of luminescence.

Acknowledgments

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